

COMBINED PERSULFATE AND CLINOPTILOLITE FOR THE REMOVAL OF COD AND SUSPENDED SOLIDS FROM A REAL DYE WASTEWATER

FAGBENRO OLUWAKEMI KEHINDE^{1, 2}, HAMIDI ABDUL AZIZ^{1, 3,*}

¹School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia (USM),
14300 Nibong Tebal, Penang, Malaysia

²Department of Civil Engineering, Faculty of Engineering and Technology, Ladoko
Akintola University of Technology, Ogbomoso, P.M.B. 4000, Nigeria

³Solid Waste Management Cluster, Engineering Campus, Universiti Sains Malaysia
(USM), 14300 Nibong Tebal, Penang, Malaysia

*Corresponding author: cehamidi@usm.my

Abstract

In the production of textile fabrics, the unfixed dye that is left in the process wastewater often show a significant influence of pollution, either in any receiving surface water or the extra burden of the pollution load in a receiving sewer. However, besides the unfixed dyes, other pollutants generated in the various stages of textile production have contributed to the strength and variability of the pollutants inherent in the resultant wastewater. Therefore, the present study characterizes a real textile wastewater and investigates the feasibility and success of the combination of persulfate and clinoptilolite in a single reactor to remove the target pollutants viz; chemical oxygen demand (COD) and suspended solids (SS). Results of the study show that the combination is feasible and successful in the treatment of recalcitrant dye wastewater. This is indicated by the removal of COD (74%) and SS (99%). The determinant factors that were observed to effectively influence the treatment process were persulfate dosage (4/1), which was standardized as a persulfate/contaminant ratio (g/g), dosage of clinoptilolite (8g), the initial pH (4) of reaction and reaction time of 30 minutes to remove COD, and 210 minutes for the removal of SS. The residual SS at 3 mg/l is within the acceptable limit of 50 mg/l, while the COD exceeded the standard limit. A biological treatment may thereafter be applied to further remove the residual COD to bring to an acceptable limit.

Keywords: Persulfate, clinoptilolite, dyes, SS, COD.

1. Introduction

Dyes and pigments are powerful colorants with a wide variety of applications. They have become indispensable materials for many industrial applications. Their applications include textile dyeing [1], colorants for plastics [2], inks and tinting used in many industries such as Artworks [3], shoe making [4], glass wares [5], cosmetics [6], paper [7], print media [8], food [9], pharmaceuticals [10], and more. Their use primarily adds color to improve appearances, make attractive and beautiful. In many situations, they are also applied to distinguish members of the same family one from another. The pharmaceuticals particularly, have situations where drugs and labels are color coded by drug class [11]. Certain drugs and their families are made with specific colors, almost as a trademark and the idea to tap the synaesthetic effects of colors [12].

Although both dyes and pigments are colorants, they are primarily differentiated by their solubility during usage. While dyes are soluble in a variety of liquids, pigments may remain as fine particles in suspension. The latter is neither soluble in water nor many solvents. In contrast to pigments, dyes have found a wider application because of their inherent properties such as solubility, availability in large number, smaller molecular sizes, ease of bonding to other materials or substances and the ease of application among others. On the other hand, pigments find more application in the artists' colors. For these reasons, dyes are encountered more in everyday life while their use in textile production and the resultant pollution effect is the focus of the present study.

The wastewater released from many industries producing or using dyes are often a source of environmental pollution. Similarly, dye wastewater generated as effluent in the process of textile production has been considered as a potential hazard to both human and aquatic life within the environment [13]. In a related study, Dey and Islam [14], stated that apart from problem to the environment, public health and aquaculture, the industrial textile wastewater also cause major havoc to ecology and agriculture. Charumathi and Das [15], also considered that textile dye wastewaters are strong colored and the discharge into receiving waters cause damage to the environment, due to the toxicity to human and aquatic life. Typically, dyes used in textile production are not all fixed to the fabrics and thus remain in the wastewater. Apart from the unfixed dyes, the pollution load in the textile dye wastewater consists of impurities washed out from the fibers, and other chemical reagents applied in the fabrics making process.

Due to the complex chemical constituent of dyes, other chemicals and materials used in the textile production process which renders the wastewater recalcitrant and non-biodegradable, treatment has often been by a combination of physical, chemical and biological methods such as; electrochemical, physicochemical, biophysical, chemical-coagulation, chemical-oxidation and several other combinations. Among the treatment methods, adsorption [16], and related techniques [17] have particularly proved to be effective as well as the advanced oxidative processes and related techniques [18]. The application of combined treatment methods such as chemical-coagulation, electrocoagulation and adsorption [19] and anaerobic, up flow anaerobic sludge blanket reactor (*UASB*) supported on alumina nanoparticles have also been applied in wastewater treatment [20].

Persulfate oxidation is a relatively newer technology in water and wastewater remediation. The persulfate anion, produced when the persulfate salt dissociates

in water is said to be a very strong oxidant but kinetically slow in oxidizing organic pollutants under ambient conditions [21]. Hence, various initiators have been used to activate and improve the persulfate kinetics to achieve better results. Some of the initiators previously used include; EDTA/Fe (III) [22], subsurface minerals [23], naturally occurring trace minerals [24], organic compounds [25], phenols [26], ultraviolet (UV) light [27], heat [28], ultrasound and heat [29]. And very recently also, clinoptilolite assisted persulfate was applied to decolorize raw textile wastewater [30]. Enhanced persulfate oxidation has been applied to remove pollutants in slurries and aqueous systems in particular. Such applications include; a tertiary treatment for the removal of pesticide acetamiprid from water [31]. To degrade chloramphenicol in water [32], in the advanced oxidation of stabilized landfill leachate [33], oxidation of paper making industrial park effluents [34], removal of bisphenol A and phosphate [35] and decolorization of CI direct Red [29], degradation of naphthol blue black in water [36].

Clinoptilolite, a common and most applied of the zeolitic family is natural and environment friendly, hence the choice as a supporting media for treatment. Its adsorptive, catalytic and ionic properties are often tapped during applications [37, 38]. Natural clinoptilolite has been applied in the adsorption of heavy metals especially [37]. They are also modified by ion-exchange to improve their properties, and hence achieve a better performance in wastewater treatment e.g. Silver-modified clinoptilolite was used to remove *Escheria coli* and heavy metals [39], CuO supported clinoptilolite towards solar photocatalytic degradation of paminophenol [40], Silver-ion-exchanged zeolite to remove bacteria and ammonia [41], adsorption of ammonium ions from landfill leachate [42], removal of Basic Blue 41 from aqueous solution [43], adsorption of Malachite Green and Rhodamine B from a dye solution [44], zeolite composite for the removal of Methyl orange, Congo red and Chromium (VI) [45], removal of Phosphate and Ammonia ions by composite clinoptilolite from wastewater [46]. Also, protection of the environment using natural zeolite has been described by Pasini, [47]. It discusses the possible exchange of cations for the removal of heavy metals and ammonium ions (NH_4^+) from both industrial and municipal wastewaters. It also shows that the structural and chemical features of zeolites make them very powerful for decontamination of waters containing radionuclides.

The present study applies a real dye wastewater generated in the production of textile fabrics. It taps the advantages of both persulfate and clinoptilolite to eliminate or to reduce the pollutant load in a real textile wastewater. It aims at investigating the feasibility and success of using simultaneously, both persulfate and clinoptilolite for the treatment of textile wastewater. While its specific objectives are to characterize the textile wastewater, investigate the removal capacity of the combined persulfate/clinoptilolite media on SS and COD and to establish the influence of basic determinant factors in the treatment process.

This study is a continuation of an earlier study on decolorization of textile wastewater using clinoptilolite and persulfate [30], but in furtherance to the earlier study, it records for the first time, the removal of SS and COD from a real textile wastewater using a combined persulfate/clinoptilolite treatment and thus its novelty. Although separate studies exist on clinoptilolite and persulfate as reviewed, there is however no record of any study on the combination (i.e. persulfate/clinoptilolite) for the removal of SS and COD in the treatment of a recalcitrant real textile dye wastewater.

2. Materials and methods

2.1. Materials and preparation

Textile dye wastewater samples were collected from an effluent discharge point of a textile manufacturing company in the north of peninsular Malaysia. Although the company runs a biological treatment plant, however, the samples used in the present study were collected as raw wastewater. 20L plastic bottles were washed and cleaned with distilled water then with the wastewater to be collected to avoid dilution. Samples were thereafter collected in the bottles and by means of a portable multi-parameter (multi-340i, Germany), the very unstable parameters such as temperature and pH were measured on the site. Samples were immediately taken to the laboratory where they were stored at 4°C prior the experiments.

The oxidant used, a sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was produced by Hamburg Chemicals and supplied as crystals in 500g (by content), tightly sealed plastic bottles. Aqueous persulfate of 1molar stock solution was prepared according to standard methods and kept at room temperature throughout the experiments. The filtrate of treated samples was obtained by passing through Qualitative filter papers (12.5cm, moderate (102)).

Although clinoptilolite was supplied in crystalline form by BIO Organics, only 2kg were prepared to the desired particle sizes (i.e., 75-250 μm), based on previous studies [48] and experiments.

2.2. Experimental procedure

Experiments were conducted in three (3) categories according to the independent variables to be investigated. The order of experimental runs by category was; determination of the influence of dosage, influence of initial pH and the influence of reaction time. Using a 250mL Erlenmeyer flask as reactor in a batch process, a standardized sample wastewater volume of 200mL was added to the reactor and same repeated for each experiment.

A predetermined dosage of persulfate (4/1), was standardized as persulfate/contaminant ratio in g/g was adopted from previous studies [49] and applied for all experiments.

Preliminary experiments were conducted prior the main experiments to establish the range of the process variable being investigated. The main experiments were conducted in the order listed above. For the determination of the influence of dosage, the sample was put into the reactors, aqueous persulfate was added followed by 2g of clinoptilolite and the reactors were agitated at a predetermined speed, by means of a laboratory orbital shaker without adjusting the pH. After 30 minutes of agitation, the reactors were removed and allowed to settle for few minutes then the supernatant were withdrawn and filtered prior analysis. The procedure was repeated for the various dosages of clinoptilolite in the particular set of experiments. Same was repeated for all other experiments but each process variable was varied per set of experiments, while keeping others constant. All experiments were conducted at ambient conditions.

The optimum dosage from the first category of experiments was applied in the subsequent sets of experiments to determine the influence of initial pH and

reaction time. Adding the same persulfate dosage to the sample wastewater, the pH was adjusted from 2-11 in separate experiments, 30 minutes reaction time and also agitated at ambient condition.

In the third and last category of experiments, the predetermined pH from the previous experiments was applied with the same dosage (as earlier) of clinoptilolite and persulfate to the wastewater in the reactor and agitated at ambient condition but at various reaction times from 30-420minutes to determine the influence of reaction time.

All experiments were repeated until there was a consistency of results, before an average of the last three were taken.

2.3. Analytical procedure

The treated sample wastewater was filtered and the aliquots withdrawn for analysis. A portion of the filtrate was analyzed for COD using the dichromate method. The treated sample was analyzed for SS content using spectrophotometer model DR 2800, after settling for 30minutes but without filtration. All procedures were based on the Standard Methods of Water and Wastewater APHA (2005).

3. Results and Discussion

3.1. Wastewater characterization

Among the dominant parameters typical of a textile wastewater, SS and COD were the main parameters of interest in the present study. Other relevant parameters such as color temperature, pH and biochemical oxygen demand (BOD) were also characterized to give background information which could assist with the understanding of the initial condition of the investigated wastewater. Table 1, presents the results of the textile wastewater characterization along with the standard for each parameter. Clearly, all but one parameter (i.e. temperature) exceeded the standard. Although the maximum value of each one of all the parameters indicated in Table 1 were far above the standard, even the averages were still in excess, indicating a highly polluted wastewater. As presented, both target pollutants i.e. SS and COD were well over 100% in excess of the standard. They both varied widely, but the initial concentrations were 250 and 2425 mg/L respectively.

Table 1. Textile wastewater characteristics before and after treatment.

Parameter	Units	Min.	Max.	Average	Standard*	After Treatment
Temp.	°C	39	41	40	40	27
BOD	mg/L	45	55	50	40	-
pH	-	11	12.4	11.7	6.0 - 9.0	-
Color	Pt.Co	2310	7100	4705	200	-
COD	mg/L	1690	2450	2070	400	643
SS	mg/L	190	742	466	200	3

Samples collected between February 2013 to January 2015

*Malaysia Environmental Quality (Industrial Effluents) Regulations 2009 (PU 9A) 434)

3.2. Investigation of treatment determinant factors

The effectiveness of the combined persulfate and clinoptilolite to remove SS and COD from textile wastewater was investigated by assessing the influence of media dosage, initial pH and reaction time.

3.2.1. Influence of dosage

Persulfate performs a chemical treatment by oxidation to remove pollutants while clinoptilolite treats by adsorption, ion-exchange and catalyzation. Clinoptilolite, apart from adsorbing the pollutant also combines with persulfate by ion-exchange and catalyzes the reaction to improve the oxidative kinetics of the persulfate. Hence, the Persulfate/c clinoptilolite media combines the properties of each individual media (i.e. persulfate and clinoptilolite) to achieve a better treatment out-put. As presented in Fig. 1, while keeping persulfate dosage constant at 4/1, clinoptilolite dosage was varied from; 2-20 g to determine the influence of dosage on the removal of COD and SS. 53 % of SS was removed at 2 g, increasing to 70 % at 8 g and up to 92 % at 20 g clinoptilolite dosage. 38% of COD was removed at 2 g, increasing to 55 % at 8 g and peaks at 64 % removal for 16 g dosage. There is a general increase in pollutant removal with an increase in the dosage. Similar to the result obtained in the present study, Shu et al. [50] and Xie et al. [51], also found that the initial concentration (i.e. dosage) of treatment media greatly influences the performance of the media. It also finds similarity in an earlier study on the investigation of persulfate dose, where a linear relationship was observed between dosage and $\log(C_{ps}/C_0)$ for all initial concentrations of persulfate, also, higher catalyst (UV dose) was required for higher persulfate dosages [52]. Although removals for all parameters continue to increase with media dosage, clinoptilolite dosage of 8 g (i.e. corresponding to the first peak with a significant increase in pollutant removal) was adopted for further experiments. The influence of a fluctuating pH could also be responsible for the variation in the pattern of removal as the media dosage is increased, hence its determination in the subsequent experiments.

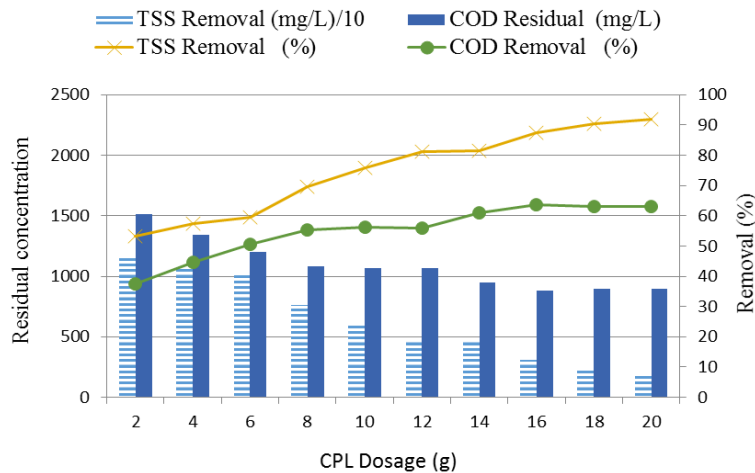


Fig. 1. Influence of dosage (S_2O_8 dose: 4/1, SS: 250 mg/L, COD: 2450 mg/L, agitation speed: 150 rpm, reaction time: 30minutes and initial pH 12).

3.2.2. Influence of solution pH

The same persulfate dosage was applied with 8g clinoptilolite (i.e. optimum from previous experiments) at varied pH, and the results are presented in Fig. 2. Generally, removals of both parameters improved with an increased pH between 2-10, but least at pH 11. However, SS removal fluctuated more in-between the pH range considered indicating the significant influence of pH in the reactions in this study. COD removal was favoured by an acidic medium, hence the best removals at pH range of 2-4 (62 % - 67 %) and near neutral pH 5-9 (61 % - 67 %). However, 53 % SS removal was good at pH 4 and better (56 %) at pH 7 but was least (3.2 %) at pH 11. It therefore shows that very basic medium is not suitable for the reaction. Although good removals were obtained in a wide range of pH, the near neutral pH 4 and 6 were better. But for the sake of uniformity, since treatment and parameter removal should be simultaneous, and to reduce the burden of neutralization as post-treatment, pH 4 was used for further experiments. Generally, decomposition of persulfate at varying pH is initiated by the catalyst (i.e., clinoptilolite) to generate sulfate radicals, followed by oxidation by the sulfate radicals [53].

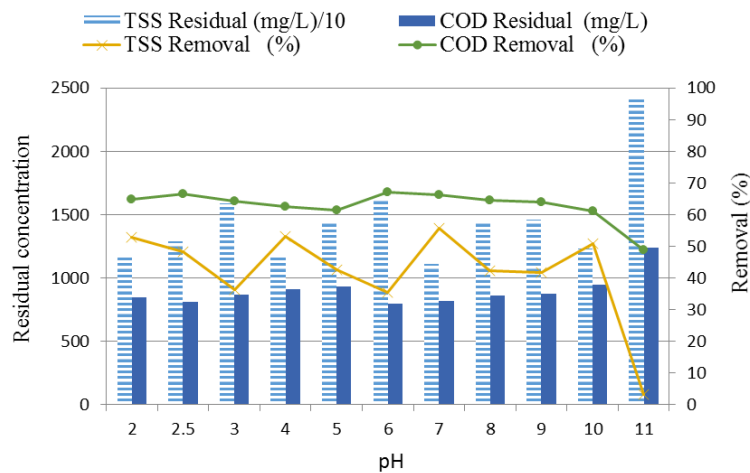


Fig. 2. Influence of initial pH of reaction (S_2O_8 : 4/1, CPL: 8g, SS: 250 mg/L, COD: 2450 mg/L, agitation speed: 150 rpm, reaction time: 30minutes).

3.2.3. Influence of contact time

Applying the predetermined dosage and pH, results of the influence of reaction time is presented in Fig. 3. Approximately 93 % SS was removed in the first 30 minutes of reaction and increased to 99 % at 210 minutes reaction. COD removal was not much influenced over the range of reaction time considered. It varied from 71 % - 74 %, and the 74 % was achieved during the first 30 minutes of reaction. It was a rather quicker reaction and removal in comparison with the reaction for SS removal. Several studies supports that there is an increase in degradation of pollutants with an increase in reaction time. Although pollutant removal increases with reaction time, the homogeneous contribution of the effect of leached active species from the catalyst (clinoptilolite in this case) may have also contributed to the pollutant degradation [54]. In a related work on the

persulfate oxidation of textile wastewater at ambient temperature, only 32 % and 71 % of COD and SS respectively were removed [55], while 73.98 % of COD was removed when activated carbon prepared from bamboo waste (BMAC) were used to treat a similar wastewater [56]. Also, in the determination of the optimal particle size range of clinoptilolite for the remediation of textile wastewater, 96 % and 62 % of SS and COD were removed [48].

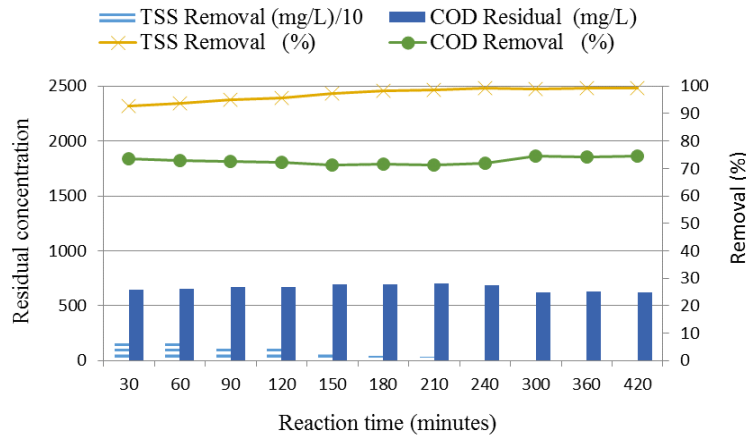


Fig. 3. Influence of reaction time (S_2O_8 : 4/1, CPL: 8g, SS: 250 mg/L, COD: 2450 mg/L, agitation speed: 150 rpm, reaction time: 30minutes, pH: 4).

4. Conclusions

The combined use of clinoptilolite and persulfate has proved feasible and successful in the remediation of a typically recalcitrant real textile dye wastewater, to render the treated water reusable in the textile processing or to be recycled for other industrial processes which do not require potable water. The success of the technique is indicated by the removal of the target pollutants of COD (74 %) at 30 minutes reaction time and SS (99 %) at 210 minutes reaction time. The determinant factors that were observed to effectively influence the treatment process were dosages of persulfate (4/1), and 8g of clinoptilolite, pH 4 as the initial pH of reaction and reaction times of 30 minutes for the removal of COD and 210 minutes for the removal of SS. The persulfate/c clinoptilolite treatment media has shown to be advantageous as it performs better in the removal of pollutant than the singular application of each process, albeit the present study has higher pollutant concentrations.

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